PHYSICOCHEMICAL CHARACTERIZATION OF Ni-Al_2O_3 AND La-PROMOTED Ni-Al_2O_3 CATALYST FOR METHANE DRY REFORMING

NORZAINI BIN ABD. RAHIM

DEGREE OF BACHELOR OF CHEMICAL ENGINEERING

UNIVERSITI MALAYSIA PAHANG

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Universiti Malaysia Pahang

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LIST OF ABBREVIATIONS

ATR	Autothermal reforming
BET	Brunauer, Emmett and teller isotherm
DR	Dry reforming
DRM	Dry reforming of methane
FTIR	Fourier transform infrared spectroscopy
GTL	Gas to liquids
IUPAC	International union of pure & applied chemistry
POX	Partial oxidation
PROX	Preferential reaction oxidation
SMSI	Strong metal-support interactions
SR	Steam reforming
TCD	Thermal conductivity detector
WGS	Water gas shift
XRD	X-ray diffraction
XRF	X-ray fluorescense

LIST OF SYMBOLS

°	Degree.
α_o	Ratio of number of gas of inelastic collisions resulting in absorption to total number of collisions of gas molecules on the surface.
c_α	Polymeric.
c_β	Filamentous.
c_γ	Graphitic.
C	Constant value, characteristic of the adsorbate.
n	Number of adsorbed molecules desorbing in unit area of the surface.
θ	Fraction of surface of covered by adsorbed molecules.
P	Gas pressure.
P_S	Saturation pressure of adsorbed gas.
S_A	Surface area of solid.
μ	Number of molecules colliding in unit time with a unit area of the surface.
V	Volume of gas adsorbed.
V_m	Volume of adsorbed gas corresponding to monolayer coverage.
$\Delta\widehat{H}_f^\circ$	Heat of formation at 25 ^{0}C and 1 atm

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CIRI-CIRI FIZIKOKIMIA Ni-Al_2O_3 DAN La-MODIFIKASI Ni-Al_2O_3 PEMANGKIN UNTUK TINDAKBALAS KIMIA ANTARA METANA-KARBON DIOKSIDA

ABSTRAK

Tindakbalas kimia antara metana (CH_4) dan karbon dioxsida (CO_2) telah dijalankan dengan menggunakan Nikel alumina sebagai pemangkin yang disediakan melalui percampuran antara nikel dan lantanum metal pada sokongan alumina pemangkin. Pemangkin 10%Ni-90% Al_2O_3 telah dimodifikasi dengan menggunakan lantaham metal yang mempunyai 3%. Fizikokimia pemangkin dianalisis dengan menggunakan seperti berikut; XRF, FTIR, BET, dan XRD untuk membandingkan diantara 10%Ni – 90%Al_2O_3 dan 3%La – 10%Ni – 90%Al_2O_3 pemangkin untuk tindakbalas kimia antara metana-karbon diokside kepada hidrogen. Melalui XRF analisis, pemangkin – pemangkin menunjukan logam utama berada dalam pemangkin tersebut dalam keadaan susunan formula yang baik seperti pemangkin yang telah dijalankan. Manakala, FTIR analisis pula mengesahkan kehadiran molekul dan pembentukan kumpulan atom dalam molekul struktur yang sama diantara pemangkin tersebut. XRD Analisis juga mengesahkan kehadiran utama kristal di dalam 10%Ni – 90%Al_2O_3 pemangkin adalah aluminate nikel ($NiAl_2O_4$) yang terbentuk disebabkan oleh tindak balas diantara Al_2O_3 dengan NiO pada suhu pengkalsinan yang lebih tinggi. Sifat-sifat fizikal 10%Ni – 90%Al_2O_3 dan 3%La – 10%Ni – 90%Al_2O_3 pemangkin menunjukkan isoterm "*Type IV*", yang mempunyai pemeluwapan kapilari dalam "*mesoporous*" dengan tenaga penjerapan yang tinggi, manakala histerisis "Type H1" mempunyai geometri liang silinder atau zarah-zarah yang berbentuk bola dengam saiz yang seragam. Analisis BET juga mengesahkan bahawa tiada kesan yang ketara di dalam luas permuakan pemangkin tersebut. Manakala purata "Horvat & Kavazoe" liang atau lubang saiz juga mennjukan tiada perubahan yang ketara yang kita dapat lihat. Berdasarkan analisis tersebut saya dapat membuat kesimpulan bahawa modifikasi pemangkin dengan lanthanum metal adalah salah satu pemangkin yang dapat mengurangkan pembetukan karbon dipermukaan pemangkin semasa proses ini berlaku.

PHYSICOCHEMICAL CHARACTERIZATION OF Ni-Al_2O_3 AND La-PROMOTED Ni-Al_2O_3 CATALYST FOR METHANE DRY REFORMING

ABSTRACT

The CO_2 reforming reaction of CH_4 was conducted by using a Ni-based catalyst were prepared by the wet co-impregnation using nickel and lanthanum on alumina support. Monometallic catalyst of 10wt.%Ni-90wt.%Al_2O_3 was promoted with 3wt.% lanthanum metal. The physicochemical of catalysts were characterized by XRF, FTIR, BET, and XRD respectively, which to compare the catalyst between the calcined catalyst of unpromoted (10wt.%Ni-90wt.%Al_2O_3) with 3La promoted (3wt.%La-10wt.%Ni-87wt.%Al_2O_3) performance for methane conversion to hydrogen. XRF analysis for the main metals presented in the calcined catalyst indicated a good agreement with the intended formula. FTIR analysis confirmed the presence of similar structural unit and formation of identical chemical moieties of the unpromoted and 3La promoted catalysts. XRD analysis confirmed the presence of major crystalline unpromoted catalysts is spinel ($NiAl_2O_4$) because it is formed by the reaction of Al_2O_3 with NiO at the higher calcination temperature of the catalyst. The physical attributes for unpromoted and 3La promoted catalyst showed a *Type IV* isotherm, in an indication typical of capillary condensation in mesoporous with high energy of adsorption and a hysteresis loop of *Type H1* under new classification system revealing cylindrical pore geometry or spheroidal particles with reasonably uniform size. BET analysis confirmed that no discernible effect for lanthanum addition to the unpromoted bimetallic catalyst. Also, the similarity between the distribution of average Horvat & Kavazoe desorption pore size for the unpromoted and 3La promoted. Based on this analysis, I can conclude that the modified catalyst with lanthanum metal is one catalyst that will be reducing the formation of carbon on the surface catalyst during this process.

CHAPTER I

INTRODUCTION

This chapter provide the general ideals on the subject that are going to be study including background of study, problem statement, research objectives, scope of proposed study, expected outcome and significance of proposed study.

1.1 Background of Study

In recent years, a lot of interests have been registered for renewable and environmental friendly energy conversion technology such as fuel cell technology application. The current crisis of depleting crude oil resources with associated environmental difficulties inspires enormous numbers of researchers around the

world to consider alternative routes for fuel production such as synthesis gas (syngas) utilization under a gas to liquids (GTL) process. However, since about 50 - 60% of the cost of this process based on the raw material (i.e. syngas) (Pena et al., 1996; Wilhelm et al., 2001), it is therefore an essential requirement to investigate the options for the production of syngas through hydrocarbons and improve them. Besides that, the low temperature fuel cell also requires continuous supply of hydrogen. Among these options, H_2-supplying reaction is via dry reforming of methane has been recently considered as a potential choice given the revolution in catalyst design and reaction operation technologies.

Methane dry reforming (DRM) is a catalytic reaction between methane and carbon dioxide to produce synthesis gas (a mixture of hydrogen and carbon monoxide). However, the main challenge that has prevented this process from commercial application is high thermodynamic potential of coke formation (Gadalla, & Bower, 1988; Hou et al., 2003; Souza et al., 2004) that deactivates the catalyst. However, the process is now being considered with high potential under the vast developments in catalyst design and reactor operation technologies with the aim to reduce carbon deposition. Based on the dry reforming reaction mechanism, carbonaceous residue mainly comes from the hydrocarbon substrate decomposition with slight contribution from a CO disproportion reaction. As a consequence coke formation on the catalyst surface weakens the activity of reaction resulting in lower conversion.

The catalysts based on the noble metals (Rh, Ru, Ir, Pt and Pb) are reportedly to exhibit better activities compared to transition metals (mainly Ni and Co), but the

high cost and limited availability hampered its industrial appeal (Souza et al., 2004). Hence it is imperative to develop alumina-supported Ni-based catalysts for DRM process due to its relatively high activity particularly at higher reaction temperature and also low cost.

Furthermore, in order to improve the carbon deposition resistance of Ni-based catalysts, various promoters such as alkaline, alkaline earth metal and rare earth are impregnated into Ni-based catalysts. In addition, the modifications to the supported catalysts by promoters in CH_4 reforming with CO_2 are common and have been reported before (Cheng et al., 2001; Xu et al., 2001; Junke et al., 2009; Yang, et al., 2010). It was reported that product ratio, selectivity and catalyst stability may improved from the modifications (Wan et al., 2007). In this study, we investigate the physicochemical characterization of Ni/Al_2O_3 and Ni/Al_2O_3 catalysts promoted with rare earth metal (Lanthanum) for methane dry reforming.

1.2 Problem Statement

In the dry reforming of methane process, one of the factors that influence catalyst activity is attributed to the high potential high thermodynamic potential towards coke formation. Through dry reforming reaction mechanism, carbonaceous residue also easily itself formed from the hydrocarbon substrate decomposition with slight contribution from a CO disproportion reaction.

Carbon formation under process can be classified into three main types, namely: poisoning, sintering and coking. While deactivation by poisoning can be eliminated by pre-treatment of the feedstock (Forzatti & Lietti, 1999; Bartholomew, 2001), particular attention to thermal operation conditions under the various stages of the catalytic reaction system is a useful approach to reduce the impact of deactivation by sintering.

In order to improve the catalytic performance, the right choices of supported catalysts are important to ensure that high activity, selectivity, longer lifetime, and thermal stability are attained. Besides that, there are other factors that could improve catalyst attributes for sintering such as the presence of strong metal-support interactions (SMSI), shape and size of the crystallite, support roughness and pore size, and additives present in the support or the metal.

Ni-based catalyst is the most popular catalyst of choice in industries. However, the deactivation occurs easily due to carbon deposition on the catalyst surface. In particular, the catalyst of choice was Ni-based because Ni metal is widely utilizes among the Group VIII transition metals that are normally preferred for reforming reaction, due to acceptable activity combined with low price and wide availability. Also, alumina (Al_2O_3) was commonly used as the support for nickel catalysts because of its high surface area, low cost and thermal stability. However, bimetallic catalysts generally show better activity selectivity, and deactivation resistance compared to monometallic catalysts in reforming reactions. In addition, to improve Ni/Al_2O_3 catalyst, the addition of a basis promoter such as lanthanum (La-

Ni/Al_20_3) could have excellent anti-coking buoyancy and stability and could enhance the thermal attributes of support.

1.3 Research Objectives

The objectives of this research are to prepare a La-promoted Ni/Al_2O_3 catalyst for dry reforming of methane and to investigate the performance of the modified La-Ni/Al_2O_3 catalyst based on the physicochemical characterization.

1.4 Scopes of Study

In order to achieve the objectives, the following scopes have been indentified:

i. Preparation and modification of catalyst using the wet co impregnation technique.
ii. To study the physicochemical properties of the Ni/Al_2O_3 and modified catalyst.

1.5 Rational and Significance of Research

In today's energy supply system, electricity, gasoline, diesel fuel, and natural gas serve as energy carries. These carriers are made by the conversion of primary

energy sources, such as coal, petroleum, underground methane, and nuclear energy, into an energy form that is easily transported and delivered in a usable form to industrial, commercial, residential, and transportation end-users. This study is significant to developments in fuel cell technologies.

CHAPTER II

LITERATURE REVIEW

This chapter provide the general ideals on the subject that are going to be study including the background and introduction of reforming process, hydrogen production from methane, dry reforming of methane and the catalysts used in this study.

2.1 Introduction

Since the beginning of the industrial revolution in the 18th century, fossil fuels in the form of coal, oil, and natural gas have powered the technology and transportation networks that drive the society. This overdependence on fossil fuels

has threatens the supply of energy and causes enormous strains to the environment (Ahmed & Krumpelt, 2001; Williams, 2002).

Today, natural gas is the preferred sources for production of syngas, a mixture of hydrogen and carbon monoxide, from which purified hydrogen can be obtained. There are several different catalytic processes for producing syngas from natural gas (Armor, 2005). Three catalytic chemical processes are used in the conversion of natural gas, composed of hydrocarbons, under a flow of high purity gaseous hydrogen. These three catalytic chemical processes are used sequentially and are described as follows; natural gas reforming, followed by water-gas shift (WGS), and finally a preferential reaction oxidation of CO (PROX).

There are basically four different types of techniques that can be used to carry out the reforming of hydrocarbon; steam reforming (SR), dry reforming (DR), autothermal reforming (ATR), and partial oxidation (POX). All these types of processes have the same purpose and lead to same final product, which is to convert natural gas, mainly composed of hydrocarbon molecules, into syngas.

2.2 Hydrogen Production from Methane

2.2.1 Steam Reforming

The process of methane steam reforming produces syngas with a ratio H_2/CO equals to 3. In this catalytic process, methane reacts with water steam in the presence

of a catalyst. The product of this reaction is syngas (Rostrup-Nielsen, 1984). The scheme of the reaction of steam reforming of methane is shown in Equation 2.1:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^{\circ}_{298} = 205 \frac{kJ}{mol} \qquad (2.1)$$

The steam reforming of methane is an endothermic process and, therefore, requires very high temperatures. Consequently, this process is relatively energy and cost intensive. Therefore, research on alternative processes of methane reforming with economic viability prospect is gaining interests.

2.2.2 Partial Oxidation

The partial oxidation (POX) of methane is a catalytic process that involves partial oxidation of methane in the presence of catalyst, and the product of this reaction is syngas with a good H_2/CO ratio (Fathi et al., 2000). The scheme of the partial oxidation of methane is shown below in Equation 2.2:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta H^{\circ}_{298} = -36.0 \frac{kJ}{mol} \qquad (2.2)$$

The partial oxidation of methane is an exothermic process. On the other hand, partial oxidation is considered an expensive process because it requires a flow of pure oxygen compared to dry reforming. Thus, there is a warning of danger that is inherent in the process of partial oxidation of methane, since the two reagents (CH_4

and O_2) can cause an explosion if the reaction is not conducted with the necessary care (Peña et al., 1996).